

# Nanoscale Stability and Dissolution of Platinum Single Crystal Surfaces in Perchloric Acid Electrolyte

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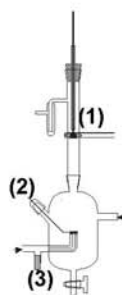
One of the most critical issues in operation of a Proton Exchange Membrane Fuel Cell (PEMFC) is the gradual degradation of the active area of platinum catalysts. To understand the degradation mechanism, we investigated dissolution of Pt (111), Pt (100) and Pt (110) single crystal electrodes at three anodic potentials directly relevant to the operation of the low temperature PEMFC. Additionally we performed the similar experiment with the (111)-(100) nanofaceted platinum surface, which is an one-dimensional model of platinum nanoparticles.

## Experimental procedure

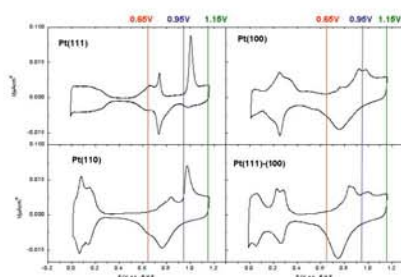
- Prepare well ordered single crystal surface using RF annealing at optimal temperature
- Determine Pt surface morphology ex situ, in exactly same area by AFM
- Clean the Pt surface before electrochemical measurement by exactly controlling annealing temperature (700°C) and time (2min) using an RF heater
- Determine surface morphology changes in the same area after potential holding by ex situ AFM

## Electrochemical setup

- 1) Pt crystal with a RF heater.
- 2) Gold counter electrode in 0.6 M perchloric acid (close to pH and non-adsorbing character of PEMFC electrolyte).
- 3) Double junction Ag/AgCl reference electrode in Luggin capillary. Solution is agitated during long-term potentiostating

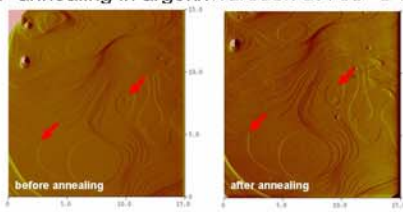


## Cyclic voltammograms of Pt single crystals in 0.6 M perchloric acid

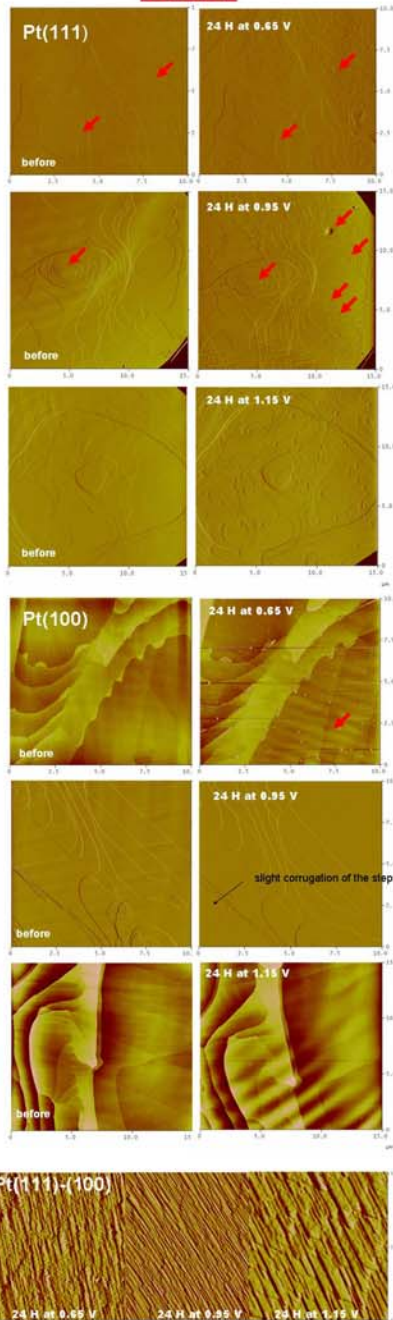


## Cleaning the surface before measurement

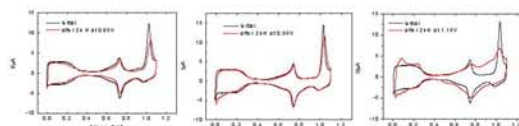
Reproducibility of Pt(111) surface morphology after RF annealing in argon/hydrogen at 700 °C for 2 min



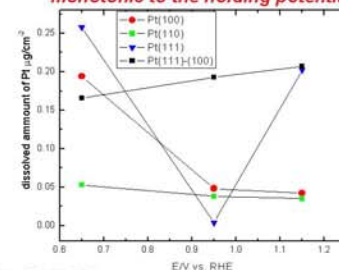
## Results



Cyclic voltammograms of Pt (111) single crystals before and after dissolution in 0.6 M perchloric acid



Pt dissolution rate is surface-specific and not monotonic to the holding potential



Pt(111), Pt(100)

**0.65 V vs. RHE:** All three basal Pt single crystals dissolve considerably. Dissolution of Pt(111) occurs at the step edge, and proceeds by layer by layer.

**0.95 V vs. RHE:** Platinum content in solution is smaller than at 0.65V. Formation of atomic pits and deep (~3.5 nm, ~1 μm wide) holes in case of Pt(111), but step corrugation in Pt(100)

**1.15V vs. RHE:** Pt(111) dissolves in "uncontrolled way" high content in solution (formation of many 0.6 nm deep rough etch holes). Pt(100) dissolves less than at two more negative potentials, surface looks almost unchanged.

**Pt(111)-(100) nanofaceted surface**

Content of platinum in solution increases with the increased potential, at 1.15 V nanofacets dissolve almost completely within 24h losing sharp features.

We performed the first atomic-scale measurements demonstrating the significance of atomic-level dissolution in the degradation of nanoparticle catalysts. Our measurements indicate that there is a potential window (~0.95 V) that all surfaces are strongly resistant to dissolution.

We will continue similar measurements with nanoparticles. We will focus on the dissolution and shape evolution of the nanoparticles. We will also use electrochemical annealing using CO cycles to see if we can restore the surfaces.

V. Komanicky, X. Wang, A. Menzel, K. C. Chang, N. Markovic, D. Myers, H. You, ECS Transactions, Volume 1, (2006) in press